CHAPTER 2
PAMS DATA IN SUPPORT OF OZONE MODELING APPLICATIONS

2.1 INTRODUCTION

Models are valuable tools that provide enormous spatial, temporal and predictive capabilities beyond the scope of monitoring networks. The use and interpretation of models are often criticized due to uncertainties in model inputs and process characterizations, as well for poor performance. The combined and complementary use of models and observations provides a more credible basis for analysis than the sum of independent analyses using models and data alone.

Support for photochemical modeling is one of several objectives targeted by the Photochemical Assessment Monitoring Station (PAMS) program. The objectives of this document are to provide example applications and recommendations for the use of PAMS data in ozone modeling applications. An emphasis is placed on the utility of PAMS type data for supporting the emissions based models (EBMs) commonly used in ozone assessment studies and State Implementation Planning (SIPs).   This document does not replace existing EPA Guidance for Urban Airshed Modeling, but should be viewed as support to improve model application studies by incorporating PAMS data.

This chapter starts with an overview of ozone modeling, followed by examples illustrating the uses of PAMS data in supporting model evaluations, developing model inputs and performing weight of evidence analyses in attainment tests. The chapter ends with a discussion on the uses and caveats on a compound by compound (or compound class) basis of PAMS measurements and their relation to model support.

2.2 MODEL OVERVIEW

Photochemical air quality simulation models (PAQSMs) used in most applications are the gridded, fixed-frame (Eulerian) systems including the UAMIV, UAMV, ROM, RADM, SAQM, CALGRID, URM and others.   All modeling systems invoke many approximations both in the description of physical and chemical processes as well as in the solution of the system of mathematical equations embodying the physics and chemistry.   The spatial extents, or "domains", of model applications often are characterized as being of urban (100-500 km), regional (500-2000 km) or super-regional (> 2000 km) scales. Gridding refers to the horizontal resolution used to delineate simulated air quality concentrations and provide detail on the emissions distribution and meteorological variables (e.g., winds and temperatures). Typical horizontal grid resolution ranges from 2-5 km and 20- 80 km for urban and regional applications, respectively. Most

models produce hourly outputs, which can be aggregated for other averaging times of interest (e.g., 8-hr, 24-hr, seasonal, annual). Models are resolved vertically (typically 5 -15 levels or more) to account for varying meteorology and emissions and to approximate vertical mixing phenomena.   Some recent systems accommodate nested or variable scale gridding schemes which allow for detailed spatial treatment in urban areas (2- 8 km) and less dense horizontal resolution in peripheral/rural portions (20-80 km) of the domain in order to optimize computational resources and apparent precision. A trend toward increasing regional-scale (or mixed regional/urban), Eulerian modeling has been apparent recently, in recognition of the interaction between regional/rural and urban areas and associated "transport" issues.

Models should be viewed as a "system" (Figure 2-1), including the meteorological and emission preprocessing models and the air quality simulation model (AQSM).   Preprocessors process raw data (i.e., emissions inventories and meteorological measurements) into the spatial and temporal fields required by the AQSM. The AQSM calculates concentration fields of air quality species (i.e., compound, element, free radical, or surrogate group), which are determined by the combined interactive effects of source emissions, mixing processes (advection and dispersion), deposition and chemical transformations.

So-called "transport" into a modeling domain is quantified through boundary conditions which are user-specified concentrations surrounding the established modeled domain (planes on each side and top), which can be brought into the domain through advection and dispersion. The AQSM includes the chemical mechanism which performs the chemical transformation calculations through highly condensed approximations (e.g., 20-50 species; 100 reactions) of the thousands of actual chemical reactions occurring in the atmosphere.   Several chemical mechanisms have been developed. They all use condensation schemes which utilize surrogate "species" for aggregating organic compounds. The carbon bond approach used in the urban airshed model (UAM) groups compounds (and parts of compounds) by bond characteristics.   Other approaches like the Statewide Air Pollution Research Center (SAPRC) mechanism use a "lumped" approach which groups compounds by similarities in reaction mechanism attributes.

These modeling systems are driven by emission inputs and often are referred to as emissions based models (EBMs), acknowledging the difference between data driven observational based models, and semi-empirical models like EKMA/OZIPM4.

Typically, a series of steps are required for all model applications:

A.   Establishment of model domain, characterization and selection of modeling episodes.

B.   Raw data gathering and processing of model inputs.

C.   Model performance and diagnostic testing, including component testing of emissions and meteorological preprocessers.

D.   Development of emission control strategies and model application and interpretation of results.

E.   Corroboration and evaluation of strategy results.

The following examples illustrate methods in which PAMS data aid the support of model evaluation and development of modeling inputs.

2.3   MODEL EVALUATION USING PAMS DATA

Two examples are presented to illustrate the use of PAMS (or PAMS-type) data in evaluating ozone modeling applications. The examples are based on field programs from the Southern California Air Quality Study (SCAQS) and the Texas-Louisiana COAST programs, both of which collected the speciated and temporally resolved data required in PAMS. The purpose of these examples are purely illustrative, to provide perspective on how PAMS can support ozone modeling.

2.3.1   Example: Los Angeles, CA

Figures 2-2 through 2-4 depict time series plots of modeled versus observed values for ozone, reactive hydrocarbon (RHC) and NO_2, respectively, based on a 1985 historical episode in Los Angeles, CA (Wallerstein et al., 1994). The figures are presented for exemplary purposes only, to show a simple plotting procedure for conducting model/measurement comparisons of ozone and precursors.

In addition to the example time-series plots, other graphical displays using tiling or isopleths could be developed to provide comprehensive, two-dimensional views relating measured and simulated data. Measured data could be superimposed on simulation maps, or side by side maps of measured and simulated results could be displayed.

2.3.2   Example: Houston Ship Channel

This example is based on a preliminary analysis trying to diagnose the cause of poor model performance using PAMS-type VOC data in Houston.   The example should be viewed as a hypothetical example of the potential value-added provided by speciated hydrocarbon data.

Several subsequent analyses of this case have suggested significant problems related to both the modeling and interpretation of results. Therefore, this example should be viewed solely for illustration, no substantive conclusions are credible.

A highly localized ozone peak of 231 ppb was observed on August 19, 1993 in Houston, Texas (Figure 2-5.) UAM-V modeling was unable to replicate timing, magnitude of the peak. A series of VOC and NO_x across-the-board emission sensitivity runs failed to improve model performance. An analysis of nearby VOC data at the Clinton site indicated an anomalous peak in the total NMHC (Figure 2-6). Through further analysis of the ambient speciation, the emission inputs were adjusted to coincide with the ambient data. Subsequent model runs resulted in improved capture of the peak ozone (Figure 2-7).

2.4   DEVELOPMENT AND TESTING OF MODEL INPUTS

2.4.1   Episode Selection and Domain Specification

Procedures for evaluating and selecting meteorological episodes for UAM SIP applications have emphasized frequency and pervasiveness of high ozone concentrations (EPA, 1991). Over the last several years perspectives on episode selection have changed, largely in recognition of the need for "richer" data bases, increasing trend toward regional analyses, and the difficulty of translating results from highly stochastic events to the form of the ozone standard. Arguably, the availability of PAMS data and other more intensive field studies (e.g., NARSTO-NE, SOS) is reasonable justification (or a prerequisite) for selecting a modeling period. A model application based on supporting precursor and upper meteorological data is more informative and credible than an application with less data. Hence, any decision matrix for episode selection is likely to contain a column indicating relative strength of supporting measurements.

Domain specifications
Almost all gridded model applications utilize regional (or greater) spatial scales to account for important mixing processes due to transport, recirculation and other processes. Consequently, any reasonable extension of modeling domains to incorporate any supporting data is advised. Similar domain adjustments would hold true for urban specific domains which are modeled with nested systems (ROM/UAM) or variable grid models (UAM-V).

Episode Selection
As discussed in Chapter 1, PAMS data assist in developing various conceptual pictures of certain attributes of episodes, such as relative influence of transport, source mix, aging of air masses, and propensity toward NO_x or VOC-limiting conditions.

2.4.2   Development of Meteorological Inputs and Meteorological Model Evaluation

The spatial and temporal attributes of meteorological data used in the specification of mixing heights (or related vertical diffusivity parameterizations) and three dimensional wind fields have substantial impact on simulating atmospheric mixing processes, and subsequent air quality and control strategy predictions. Perturbations in either mixing height or wind fields have been shown to change both the level of precursor control as well as the preferred direction (i.e., VOC or NO_x) of control needed to demonstrate attainment (Sistla et al., 1994; Sistla et al, 1996). Although different meteorological modeling approaches can produce disparate results, the availability of high quality meteorological data should reduce differences in simulation results among various techniques.

The historical shortage of quality upper meteorological data, often limited to twice daily FAA soundings in one (or nearby) domain based location, has created concern in several UAM applications. The PAMS requirement for upper meteorological monitoring is potentially a major contribution toward improving model applications. PAMS minimum requirements specify 4 soundings per day of winds and temperature. While rawinsondes can be used to meet these requirements, automated remote sensing techniques such as Radar/Sodar wind profilers and Radio Acoustic Sounding Systems (RASS) offer enormous spatial (50-100 m increments, vertical Z-space) and temporal (hourly) resolution, and are used as a basis for subsequent discussions. Wind and temperature fields with greater temporal resolution should reduce much of the uncertainty associated with growth of the surface-based mixed layer, particularly during the rapid growth, late morning transition period. PAMS upper meteorological monitoring requirements reflect a commitment in the right direction toward enhancing modeling efforts. The PAMS contribution of 1 upper meteorological monitoring site per PAMS network is a foundation for developing spatially (horizontal) representative monitoring networks capable of characterizing regional gradients in mixing height and wind fields.

The following discussion focuses on the ability to improve wind and mixing depth fields brought about by the PAMS upper meteorological monitoring requirements, with an emphasis on the use of continuously operating radar profiler and RASS instrumentation. (More detailed discussions regarding the use of PAMS meteorological data are found in Dye, 1995.)

2.4.3 Mixing depth

Mixing (and associated dilution/concentration) of ozone and precursors throughout an episode impacts ozone concentrations, and subsequent control strategy calculations. Characterization of the mixed layer throughout the morning to afternoon growth period may be just as important as estimating maximum late-afternoon mixing depth. Continuously operating radar and RASS profilers provide a means to depict this growth with improved temporal and spatial (vertical) resolution. Particularly promising mixing height applications based on the use of Radar profiler reflectivity coefficients, C_n^2, should provide a strong complement to RASS

temperature profiles for characterizing mixing heights.

Advantages of Radar profiler and RASS

Information produced by profilers/sodars and RASS will improve characterization of the mixed layer depth. Both the temperature profilers produced by RASS and C_n^2 coefficients have temporal resolution of at least one hour enabling improved description of diurnal mixing depth development, a vast improvement over the twice daily FAA soundings. The use of C_n^2 is particularly attractive, as it is a direct indicator of mixing depth. Comparisons between aircraft measurements and C_n^2 (Figure 2-8) suggest that C_n^2 adequately tracks mixing depth. As profiler and RASS data from recently installed sites continues to be processed and reviewed, an improved understanding of the strengths and limitations of remote sensing techniques under different meteorological conditions will evolve. Currently, these methods suggest outstanding potential for characterizing mixing and advection processes for modeling applications in the lower troposphere.

The ability of C_n^2 to depict the diurnal mixed layer growth for July 12 and 13 is shown clearly in Figure 2-9. The slower growth on the second day coincided with higher ozone concentrations, suggesting that reproducing the temporal growth of the mixed layer is a model sensitive component.

The potential value of C_n^2, relative to RASS also is illustrated in Figure 2-10. Penetration of RASS often is limited to about 1000m, falling short of many typical daytime mixing depths which often exceed 2000 m. Radar profilers penetrate well beyond the well-mixed layer. Consequently, reflectivity values provided by profilers extend to high afternoon elevations of the mixed layer that are beyond the scope of RASS. Some caution regarding the representativeness of C_n^2 during night is warranted given the relatively high nighttime values.

2.4.4 Wind fields

Wind fields strongly influence the outcome and interpretation modeling results. Given that most of the air volume under consideration in any application is strongly influenced by upper air flows, the importance of characterizing vertical wind field gradients should not be understated. Upper air flow characterization dictates much of the "direct"source-receptor relationships, as well as the degree of mixing and attendant effects on atmospheric chemistry. The implementation of continuous operating sodars and radar profilers is a major improvement, providing more resolved time and space (vertical) data to better reproduce the most fundamental modeling inputs.

Additional surface stations and a local upper air station will improve the representativeness of the processed wind fields. Previously, twice-daily soundings from the nearest or most representative FAA location provided the raw data for vertical wind profiles. PAMS requirements will insure the operation of at least one upper meteorological site within an

"urban" scale domain.

Advantages of remote sensing instrumentation

Remote sensing instruments such as profilers/sodars and RASS provide a means to characterize wind flow phenomena, and often are capable of resolving various meteorological phenomena including land-sea breeze regimes, recirculation patterns and nighttime jet formation. Figure 2-11 displays an analysis of output from a radar profiler in the Northeast U.S. over a 2-day period. Various phenomena are superimposed on the diagram, based mostly on interpretation of the wind data. While the wind data (speed and direction) form the basis for direct input into meteorological models like the UAM Diagnostic Wind Model, the ability of profiler data to enable interpretation of low-level jets and mixing depths sets provide phenomena for comparison with meteorological models.

Graphical comparisons between simulated wind fields and remote sensing data should be produced for those episodes incorporating upper meteorological data. Modeled wind fields plotted in a manner compatible with that displayed in Figure 2-11 can be compared visually with observed wind fields. These comparisons should include 1-dimensional (vertical) site by site comparisons of several vertical levels and time periods, covering important temporal transition periods. Two-dimensional (horizontal) comparisons between profiler outputs and simulated wind fields for surface and elevated layers be produced to evaluate the model's ability to replicate observed horizontal gradients.

2.4.5   Additional uses for PAMS meteorological data

Upper air temperature profiles

As discussed above, the RASS vertical temperature profiles provide increased vertical and temporal resolution for estimating mixing depths. Additionally, temperature profiles are required for atmospheric chemistry calculations performed within the chemical mechanisms

Solar and UV Radiation

PAMS requires measurements of total solar (.10 to 4.0 μm) and UV (0.10 to 0.40 μm) radiation. The photolytic reactions are strongly sensitive to UV, and such measurements could be used for calculating photolysis rates of key reactions. However, calculation of photolysis rate constants often is automated within different modeling codes. UAM-IV, for example, assumes bright sky conditions and sun position (spatial/temporal coordinates) for internal calculation of photolysis rates. The UV data should be used whenever available they provide a more realistic representation of the physics driving atmospheric chemistry routines in the AQSMs. Future modeling guidance will need to address the use of radiation measurements.

Relative Humidity

Water vapor plays an important role in ozone formation, and relative humidity (in combination with temperature) can be utilized to estimate water concentrations. Relative humidity is a critically important parameter for estimating visibility impairment, and should prove valuable in future fine particle and visibility modeling applications.

Development of Boundary and Initial Conditions

The use of air quality data for developing initial and boundary conditions is largely an iterative process coupled closely with model evaluation concepts discussed above. The spatial coverage provided by PAMS is not adequate to develop comprehensive sets of air quality model inputs. Consequently, the available data are best suited to evaluating initial and boundary inputs used to drive the model simulation. Over the last ten years the spatial and temporal limits have been expanded for most model applications, partly because extended simulations are less sensitive to initial conditions. Therefore, this document places much greater emphasis on the use of data for evaluation purposes rather than input development. Nevertheless, PAMS-type data should be used for examining air quality inputs, especially boundary conditions which are a critical component of any simulation.

For most urban scale model applications, one (or possibly two) Type I "upwind" sites will be available for examination of boundary values. All of the comments regarding compensating errors, the advantages of reducing degrees of freedom for general model evaluation apply equally for evaluation of boundary conditions. Although it is important to quantify boundary ozone (supported by PAMS Type 1 sites), measurements of NMOC, NO_x and carbonyls add strong value to characterizing boundary conditions. Boundary conditions and transport are closely related, in the sense that transport phenomena are quantified as boundary values in a model application. Transport involves several factors in addition to the "additive" effect of incoming ozone. Transport includes movement of precursors or precursor "sinks" such as PAN and N_2O_5 which under certain conditions can release NO_x. The role of ozone transported from an upwind location and acting as a radical initiator downwind (ozone is the dominant source of hydroxyl radicals) is a component of transport, in addition to a strictly additive role of imported ozone.

2.5 DEVELOPMENT AND EVALUATION OF EMISSIONS INPUTS

The PAMS speciated NMOC data provide strong support for modeling by enabling evaluation of the emission inputs driving models. The reader is referred to Chapter 3 for examples of the use of PAMS data in evaluating emissions.

2.6 DISCUSSION OF PAQSM PERFORMANCE AND CORRESPONDING USES OF PAMS AIR QUALITY DATA

Traditional ozone model evaluations have relied on operational evaluations comparing surface ozone observations with modeled ozone predictions. Ozone models often produce reasonable surface level spatial and temporal reproductions of observed ozone fields. However, the use of ozone as the sole indicator of model performance/behavior can produce misleading confidence in the model's ability to correctly predict response to other meteorological episodes, or more importantly, emission reduction scenarios.

2.6.1 PAMS and Compensating Errors

Ozone is a secondarily formed pollutant with concentrations dependent on many factors many combinations of which could lead to similar ozone. Various combinations of compensating errors can produce apparently "correct" ozone fields for wrong reasons. The chance that the model is reproducing ozone for the "right" reasons may or may not be greater than the chance that some combination of compensating errors is responsible. For example, underestimates of emissions can be compensated by restricted mixing through underestimates of mixing heights or wind speeds. The complexity of the coupling of meteorological, emissions, deposition and transformation processes introduces numerous opportunities for compensating errors, and renders a very difficult identification of those processes and factors involved in compensation.

The issue underlying compensating errors is that models are applied in a prospective predictive mode with an assumed confidence, built on operational evaluation of ozone, that the physical and chemical processes are adequately characterized and therefore the model will respond correctly to emission perturbations. However, an operational evaluation only assures that surface ozone is estimated reasonably well under the existing model input scenario, a phenomenon resulting from either (1) adequate characterization of physical/chemical processes or (2) the operation of compensating errors. Because so many non-linearities exist, encountering a "flaw" in the modeling system may not happen until rather aggressive control scenarios are imposed which can not be evaluated because the testing of "projected" emission control experiments is impossible. Consequently, the model could produce misleading, and even misdirected, conclusions regarding control strategies.

The influence of compensating effects may or may not lead to incorrect conclusions regarding control strategy analysis. But the assumption that compensating errors are not present and processes are characterized appropriately because of a successful operational evaluation is not valid. A prevailing consensus does not exist on the frequency and importance of significant compensating errors in current applications.

2.6.2 Suggested Uses of PAMS Data for Model Evaluation by Compound Class

The previous discussion on compensating errors is a logical lead-in to describing the value

of PAMS data in support of the model evaluation process. Compensating errors are related to degrees of freedom within a system.   Fewer data categories result in a less constrained evaluation system and consequently increase the likelihood of a strong compensating error effect. The availability of additional measurements beyond surface ozone restricts the overall freedom for " model calibration" and similarly reduces the propensity toward compensation. A simulation exhibiting good agreement with ozone and precursors would yield far greater confidence that the model is working properly, than with the use of surface ozone only.   Hence, the intrinsic value of incorporating precursor data in the model evaluation process is the potential for reducing compensating errors in the modeling system.

The following sections discuss and provide examples of the use of subclasses of PAMS data in model evaluations. Somewhat more emphasis is placed on caveats associated with the data in order to forewarn the user to prevent inappropriate model-data comparisons. Any comparison of measured air quality and simulated air quality reflects the cumulative effects due to various physical/chemical processes. Insight on the relationship between physical and chemical processes and associated measurements should be used to guide the types of analyses performed on the available data. Certain types of data may be subject to greater relative influence from a specific process (e.g., less reactive NMHC and emissions), as opposed to other measurements subject to multiple processes (e.g., ozone affected by emissions, meteorology and photochemistry).

Model-measurement comparisons should`make full use of the spatial and temporal ranges available in the measured data. In addition to the station by station time-series plots, 2-dimensional spatial displays during selected time periods using isopleths, tiling, or other displays should be produced to convey a sense spatial representativeness replicated by the model. Extreme care should be exerted since the sparse spatial density of PAMS sites could create misleading depictions of the true atmospheric state.

2.6.3   Total NMOC and NMHC

Comparisons of PAMS data with a corresponding estimate of modeled aggregate non-methane organic compounds (NMOC) provide a means to determine if the modeling system is capable of characterizing precursor/VOC levels. The limitations and definitions of both measured NMOC and modeled NMOC must be understood in order to develop logical comparisons. The definition of the sum of compounds reported as measured NMOC are likely to never match an analogous definition for modeled NMOC. This discrepancy is due both to the variety of "measured" NMOC definitions and the various NMOC condensation schemes incorporated in chemical mechanisms.   Such differences do not preclude model/observation comparisons, but they must be understood to explain the fraction of disagreement not attributed to model error.

Measurement/reporting Issues.

Measured NMOC is not a clearly defined term, and varies with reporting procedures, instrumentation and instrument technique**.** The precise definition of NMOC is all organic compounds minus methane. The closest measured approximation from a typical PAMS site would include all compounds from both GC and cartridge techniques (carbonyls are NMOC). However, the NMOC reported to AIRS typically is the list of 56 or so targeted species based on Gas Chromatograph (GC) measurements. The targeted species are but a subset of all the species that elute through a GC column. Sometimes the cumulative areas under all peaks are reported as NMOC. Different instruments and techniques have substantial impacts on GC derived NMOC, adding an additional source of inconsistency concerning NMOC data reporting. For example, the loss of many oxygenated and polar acting species, including biogenic compounds (e.g., monoterpenes), associated with sample pretreatment and water management is system dependent. Generally, as sampling methods and GC instruments and techniques improve, more compounds, including carbonyl species, will be captured and passed though to the detector. This is desirable progress, but an accounting of the different techniques, changes in methods, etc. must be available to provide a basic understanding of what measured NMOC represents. Further complicating this issue is the uneven detector response to different organic compounds. These issues are especially important with respect to trends analyses.

Carbonyls can account for 30% or more of the total NMOC, yet a much smaller fraction is reported as PAMS requires the reporting of only three compounds: acetone, formaldehyde and acetaldehyde. Numerous issues are associated with carbonyl sampling and analysis as with any monitoring technique. These measurement related issues are not intended to discourage model/ambient comparisons. However, clear understanding of what is measured/reported will improve the interpretation of model/ambient comparisons.

Simulated NMOC and NMHC

Thousands of reactions and hundreds of species are required to explicitly characterize the atmospheric chemistry phenomena responsible for ozone formation. The inclusion of so many reactions and species would extract an enormous computational burden; consequently, PAQSMs utilize chemical mechanisms which condense the number reactions and species down to manageable levels. Typically, the inorganic species and reactions (e.g., principal NO_x and ozone reactions) are treated explicitly. However, the organic chemistry is highly parameterized with several "surrogate" species used to represent compound classes, bond types or other functional relationships. Aggregating all of the modeled VOC groups represents an approximation of NMOC. However, given the limitations of carbonyl measurements as well as the model's treatment (or lack of) numerous carbonyl compounds, more meaningful model/data comparisons would be conducted with estimates of non-methane hydrocarbon compounds (NMHC). In most chemical mechanisms, hydrocarbon groups are differentiated from oxygen containing organic groups allowing for an adequate aggregation to represent NMHC. As discussed earlier, an

understanding of what is actually measured and reported is a prerequisite for conducting comparisons.

2.6.4   Speciated VOC and Carbonyls (Isoprene and Formaldehyde)

Comparisons between modeled and measured species are limited by the model's ability to depict explicit species. Explicit organic species in the CB4 mechanism are formaldehyde, isoprene, ethanol and methanol.   Comparisons with both formaldehyde[1] and isoprene are strongly recommended, given the potential value both species provide in characterizing important photochemical and natural emissions processes. Isoprene is the most important biogenic emission precursor specie. In the Eastern U.S., the suspected levels of biogenic emissions are so large that any observed corroboration of their predictability is worthwhile.   The level of biogenic emissions influences the relative need for NO_x or VOC control strategies. Although isoprene is reactive, the emission levels are so large that resulting ambient levels (> 1 ppb) should provide a reasonable basis for comparison between modeled and observed levels.

Formaldehyde is emitted directly as a primary species, formed secondarily, and undergoes photolysis.   Although formaldehyde may not act as a surrogate for other carbonyl species, the observed levels, chemical reactivity and multiple activities suggest that formaldehyde is an important indicator of model performance.

2.6.5   Nitrogen: NO_x (NO, NO2), NO_y

Comparisons of NO, NO_2 and total oxidized nitrogen (NO_y) with corresponding modeled estimates provide a basis for corroborating the NO_x emissions component and atmospheric chemistry phenomena. Comparisons of the diurnal pattern of NO concentrations are influenced mainly by proximity of NO_x emission sources, particular during the morning hours. The titration of ozone due to NO_x emissions diminishes during the day as NO is oxidized to various products.

Total NO_y comparisons, assuming measured NO_y are available, complement NO comparisons.   During periods when NO_x is most likely to reduce ambient ozone, NO constitutes the major fraction of NO_y. However, as oxidation processes proceed, emitted NO eventually transforms into other more highly oxidized species (NO_2, nitric acid and PAN) which are major components of NO_y. In fact, the ratio NO/NO_y is a useful metric for comparison as it provides a relative measure of air mass aging, higher ratios reflecting air laden with "fresh" NO_x emissions. Total NO_y measurements should account for NO_x, HNO_3, PAN, and organic nitrates, many of which are semi-volatile and exist in the particle phases; species typically not accounted for in most

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[1] Certain parts of various olefin compounds are aggregated as Formaldehyde in the CB4 mechanism. Thus, the modeled formaldehyde will always be somewhat higher than "true" simulated formaldehyde.

chemical mechanisms. Thus, some unknown amount of negative (underestimate) bias due to organic nitrate species that are not modeled is present. Nevertheless, on balance modeled NO_y (sum of NO_x, HNO_3 and PAN) probably is subject to similar difficulties associated with using modeled NMHC as a basis for comparison with ambient data, and should be considered a useful, albeit rough estimate of total NO_y.

Comparisons with NO_2 provide a strong test of model's ability to capture the timing and magnitude of atmospheric chemistry phenomena, given the central role that NO_2 plays in oxidant chemistry. Unfortunately, NO_2 measurements rarely are available, limited to a few select research grade efforts in special field studies. NO_2 data reported from most monitoring sites are reported as the difference between measured NO_x and NO. The chemiluminescence technique for measuring NO_x and NO is more reliable for NO. However, the total NO_x measurement, which typically requires conversion of NO_2 to NO through a molybdenum catalyst, is subject to strong, positive interferences from other NO_y species (e.g., HNO3, PAN). Thus, the NO_x measurement is believed to be reside somewhere between actual NO_x and total NO_y.

2.7   USE OF PAMS DATA TO CORROBORATE MODELED STRATEGIES

Modeled attainment demonstrations require one to project emissions and corresponding air quality estimates several years into the future to a statutory attainment date. Model predictions are then compared to the national ambient air quality standard (NAAQS) to determine whether the simulated control strategy is likely to be sufficient to meet the NAAQS. This latter exercise is referred to as a "modeled attainment test".

There are substantial uncertainties inherent in modeled attainment demonstrations. These arise from uncertainties in the data bases driving the model, approximations of chemical/physical processes made in the model's formulation and uncertainties about a number of factors affecting emission projections. In recognition of these uncertainties, future modeled attainment tests are likely to incorporate a "weight of evidence" concept to assess adequacy of a proposed emission control strategy. In a weight of evidence analysis, air quality modeling results serve as one (perhaps the most important) element. Other elements include a series of corroborative analyses, many of which will draw on the kinds of data produced by the PAMS network. Table 2-1 illustrates elements which would be considered in a typical weight of evidence analysis. The middle column in the table identifies factors which affect the credence or "weight" given to a particular element. The right-hand column describes outcomes which would be consistent with concluding that the attainment test is passed despite air quality modeling results which do not quite show attainment.

Looking at the elements in Table 2-1, there are a number of potential uses for PAMS data. For example, we see that the more extensive the (air quality) data base used to formulate inputs to and evaluate performance of the photochemical grid model, the greater the weight that can be

assigned to its results. Looking at the trend data element, we see that presence of precursor trends which are consistent with apparent ozone trends would lend weight to results of the trend analysis. Other trend analyses may be used as means for assessing model performance, thereby affecting weight assigned to modeling in subsequent "mid-course reviews" of strategies prior to the statutory attainment date. For example, as noted in Chapter 4, observed trends in ratios of indicator species like $HCHO/NO_y$ or trends in highly reactive to less reactive VOC species may be compared to model predictions to help assess model performance. Good performance would increase the weight given to modeled results in the attainment test. Table 2.1 also shows how results produced from observational models would be used in a weight of evidence analysis. The term "observational models" in Table 2-1 includes "receptor models" (Chapter 3, this report) as well as the observational models described in Chapter 4. The principal value of the observational models is to provide qualitative indicators of which strategies are likely to be most effective in reducing future ozone levels. Thus, they may be used to corroborate whether a proposed strategy simulated with a photochemical grid model is addressing the appropriate classes of sources. PAMS data are also of potential use for the "selected episodes" element in the weight of evidence analysis. As described in Chapter 1, the PAMS data base will provide much more extensive information about meteorological conditions aloft than is currently available. Because conditions aloft are believed to be important factors affecting observed surface ozone concentrations, this information might be used to good effect in helping us to identify distinctive meteorological regimes leading to high ozone. This will provide increased confidence that we are considering the important regimes corresponding to high ozone, thereby increasing the weight given to the estimated severity of selected episodes in the weight of evidence analysis.

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Air Quality Modeling System

Air Quality Fields
ICs/BCs

Meteorological
Model

Emissions
Model

Meteorological
Fields

Emissions Fields

AQSM

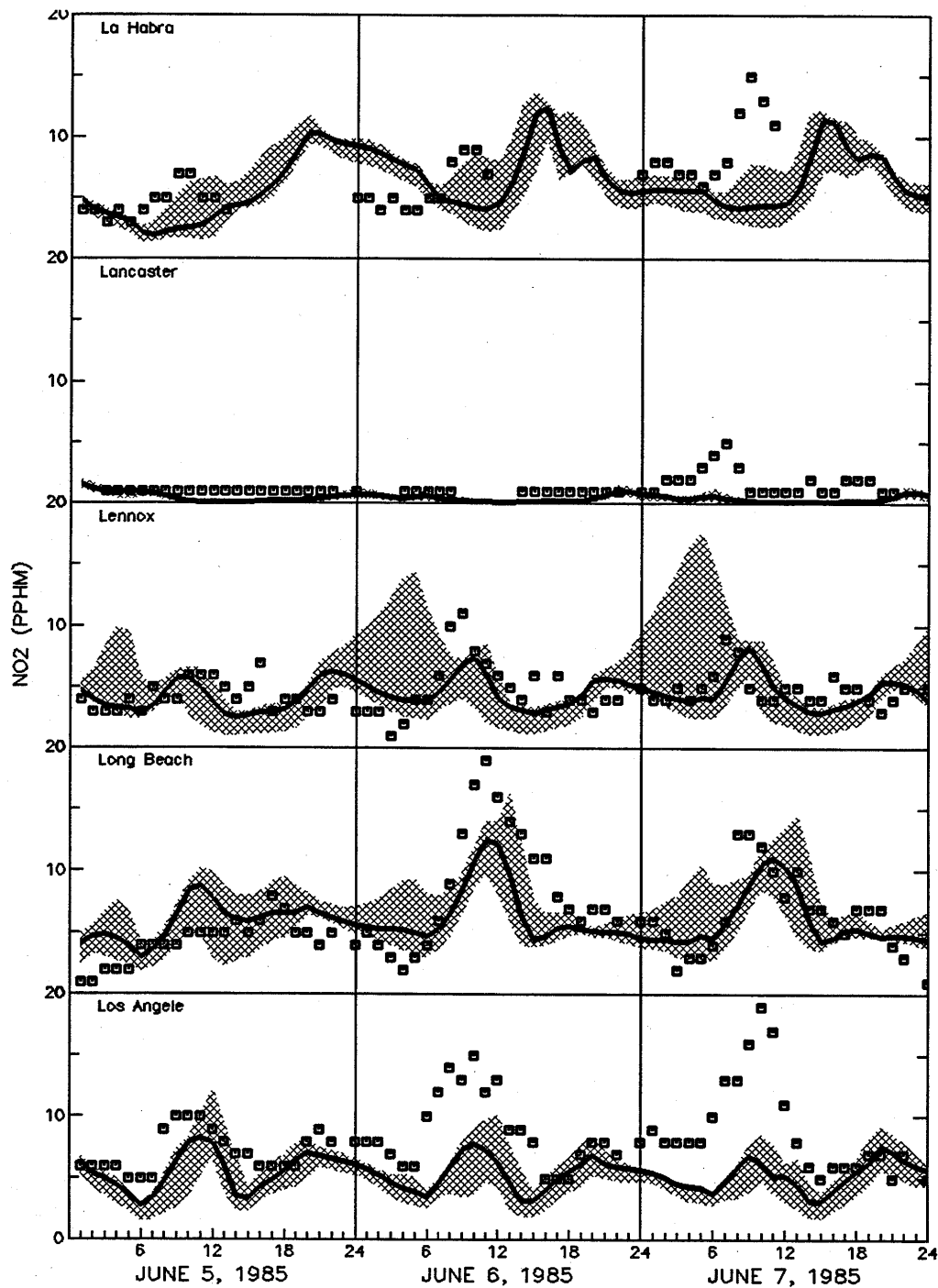Ambient Concentrations
Deposition levels
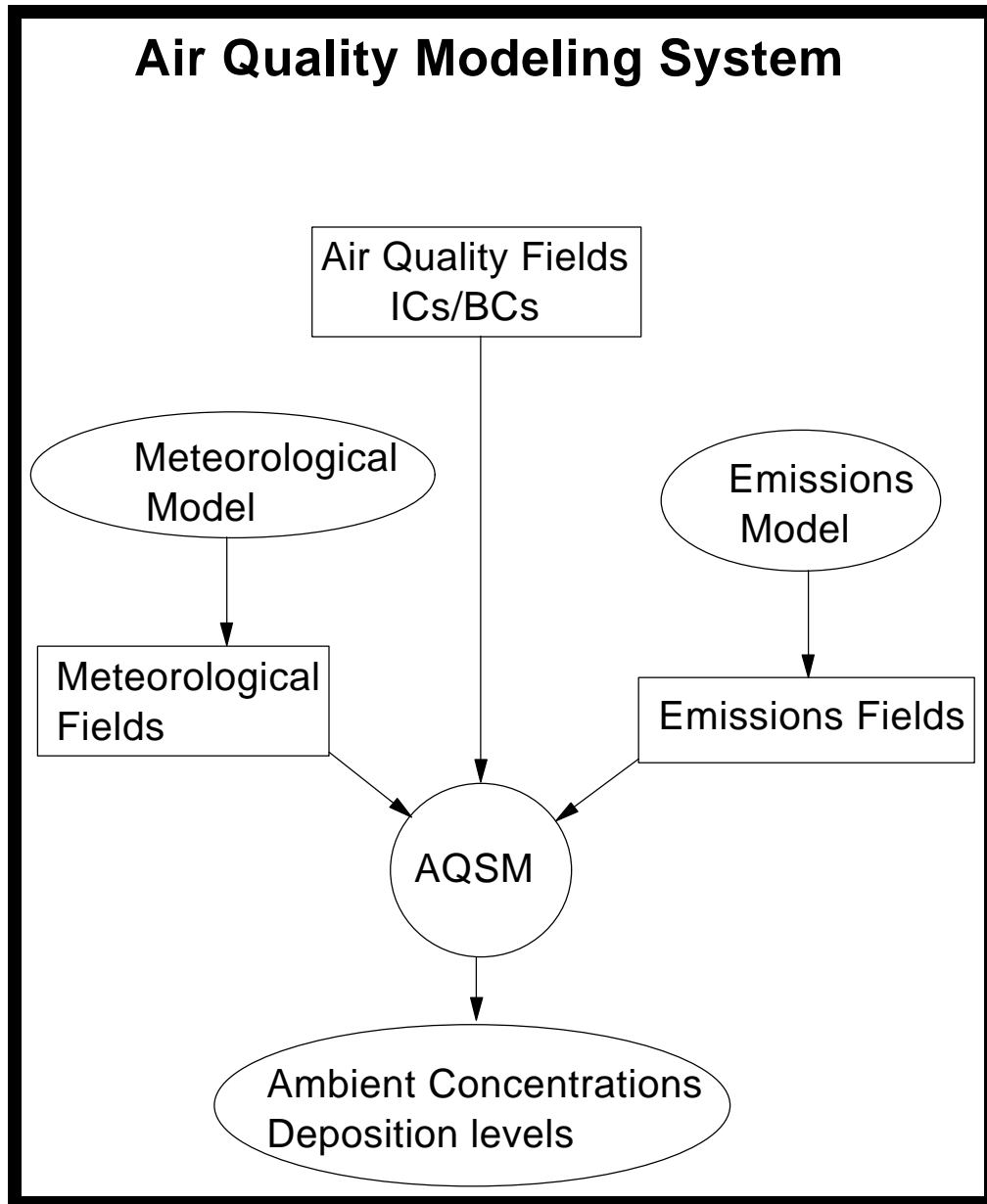
**Figure 2-1.** Schematic of air quality modeling system.
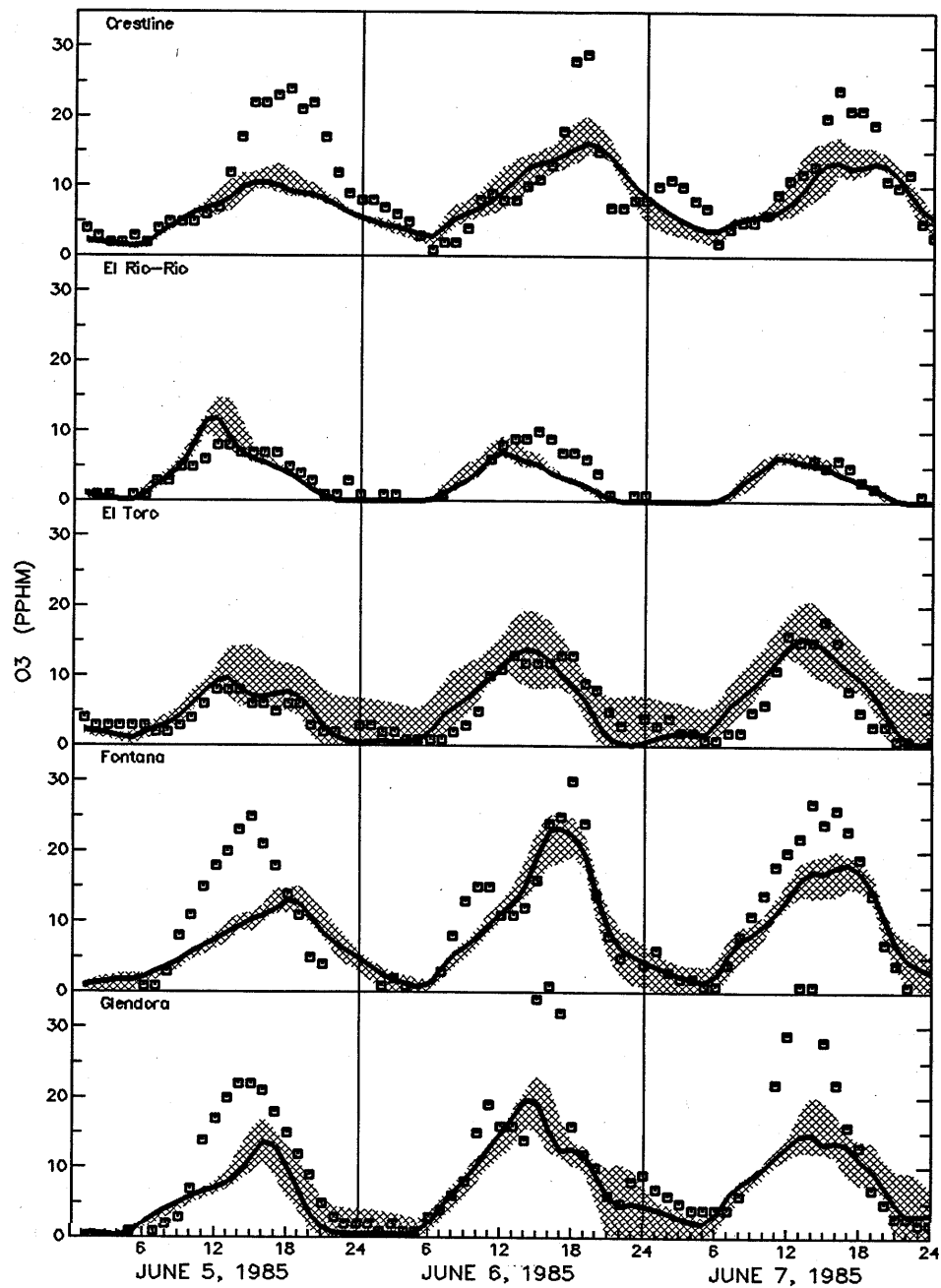
Figure 2-2. Comparison between predicted and measured ozone concentrations for June 5-7, 1985 in the South Coast Air Basin (Wallerstein et al., 1994). The solid line = distance-weighted mean value (average of 4 grid cells), shaded area=maximum and minimum value of the 9 cells around the station. Observed values are squares.

Figure 2-3. Comparison between predicted and measured NO$_2$ concentrations for June 5-7, 1985 in the South Coast Air Basin (Wallerstein et al., 1994). The solid line = distance-weighted mean value (average of 4 grid cells), shaded area=maximum and minimum value of the 9 cells around the station. Observed values are squares.
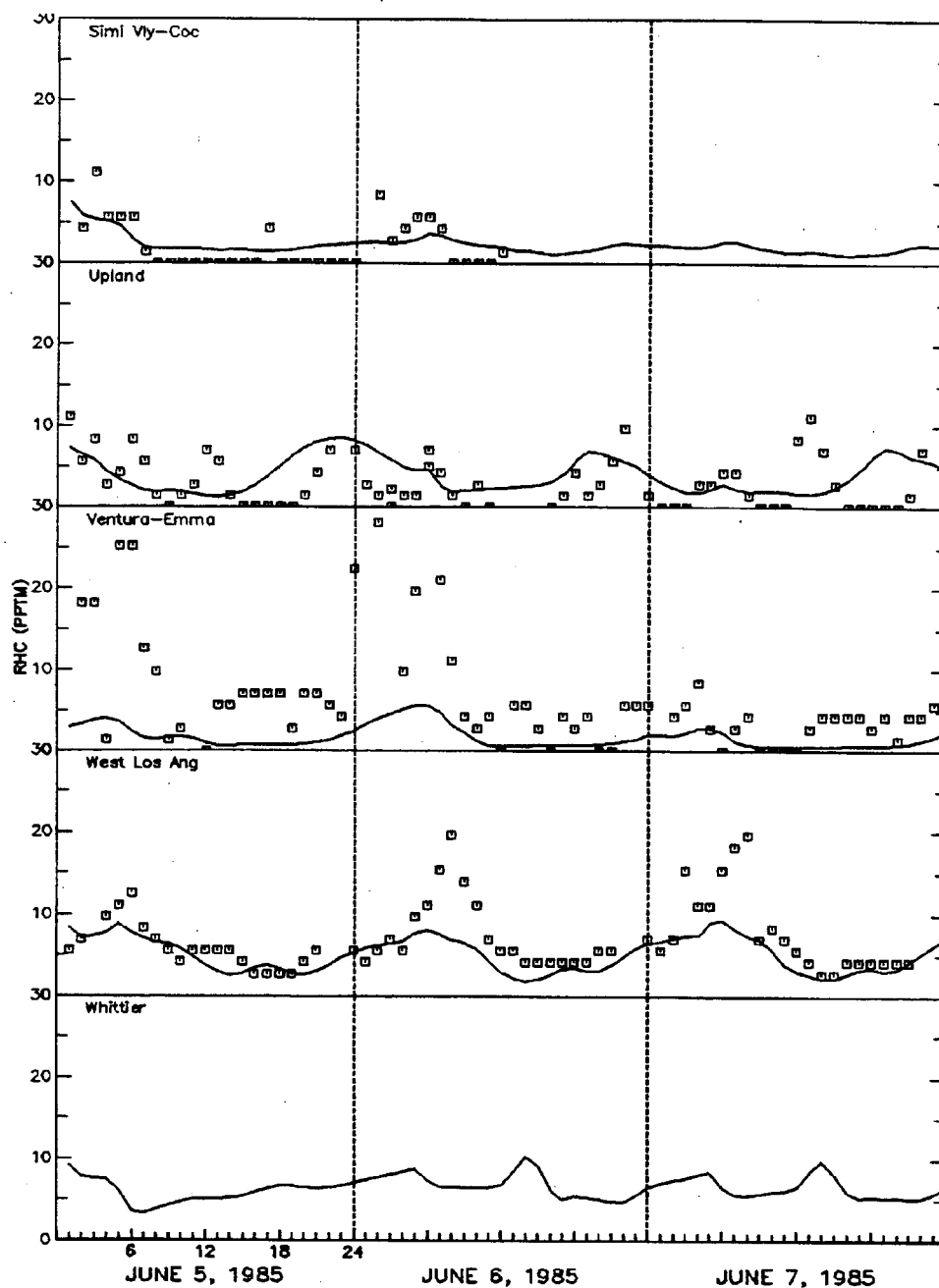
Figure 2-4. Comparison between predicted and measured reactive hydrocarbon (RHC) concentrations for June 5, 6, and 7, 1985 in the South Coast Air basin of Claifornia (Wallerstein et al., 1994) The solid line = distance weighted mean value (i.e., average of 4 grid cells).
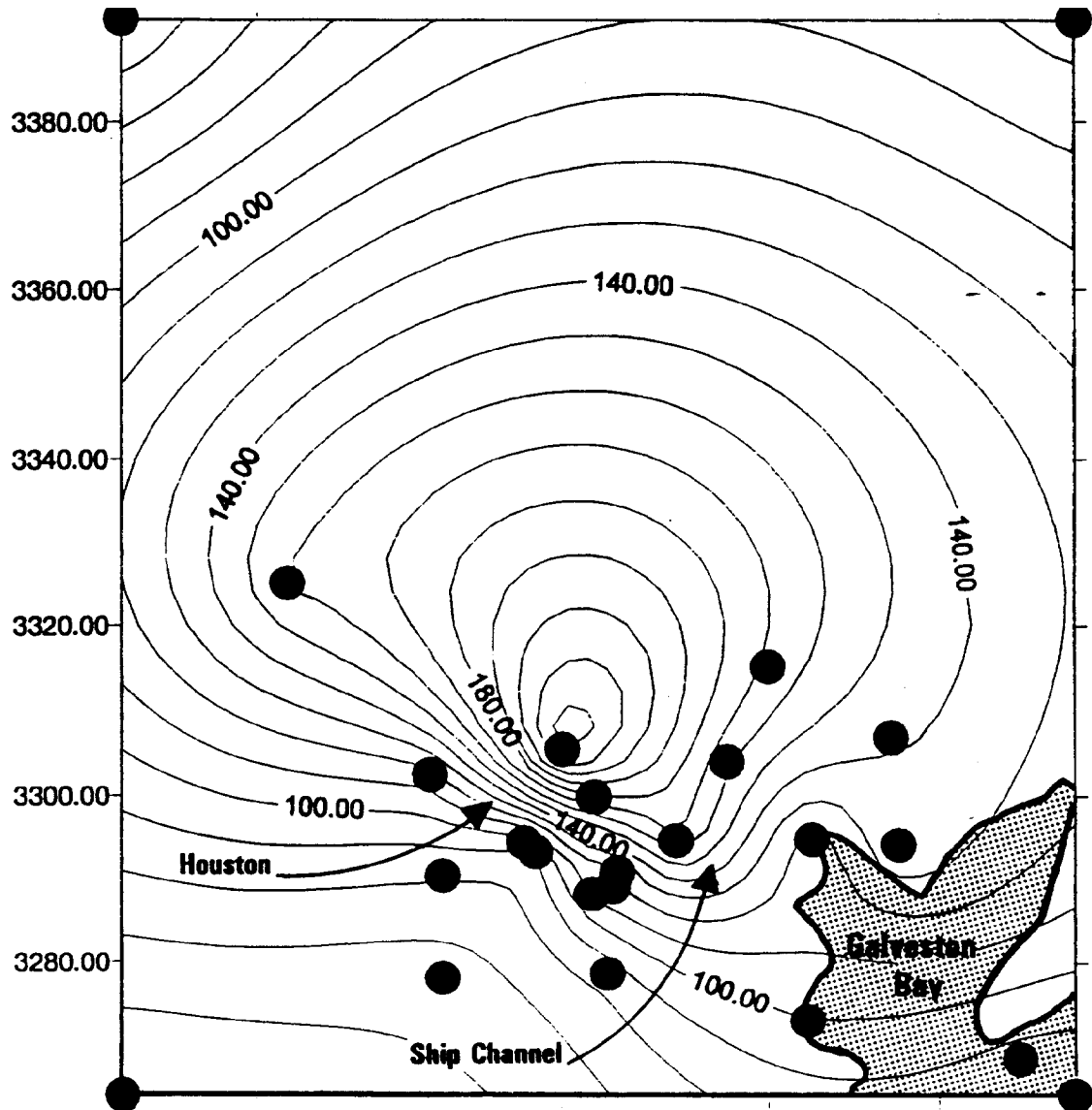
Figure 2-5. Ambient isopleths of surface level ozone for Houston, TX on August 19, 1993 (SAI, 1995?).

Figure 2-6. Ambient NMHC measured at the Clinton, TX site for August 17-19, 1993 (SAI, 1995)

NMHC AT CLINTON SITE
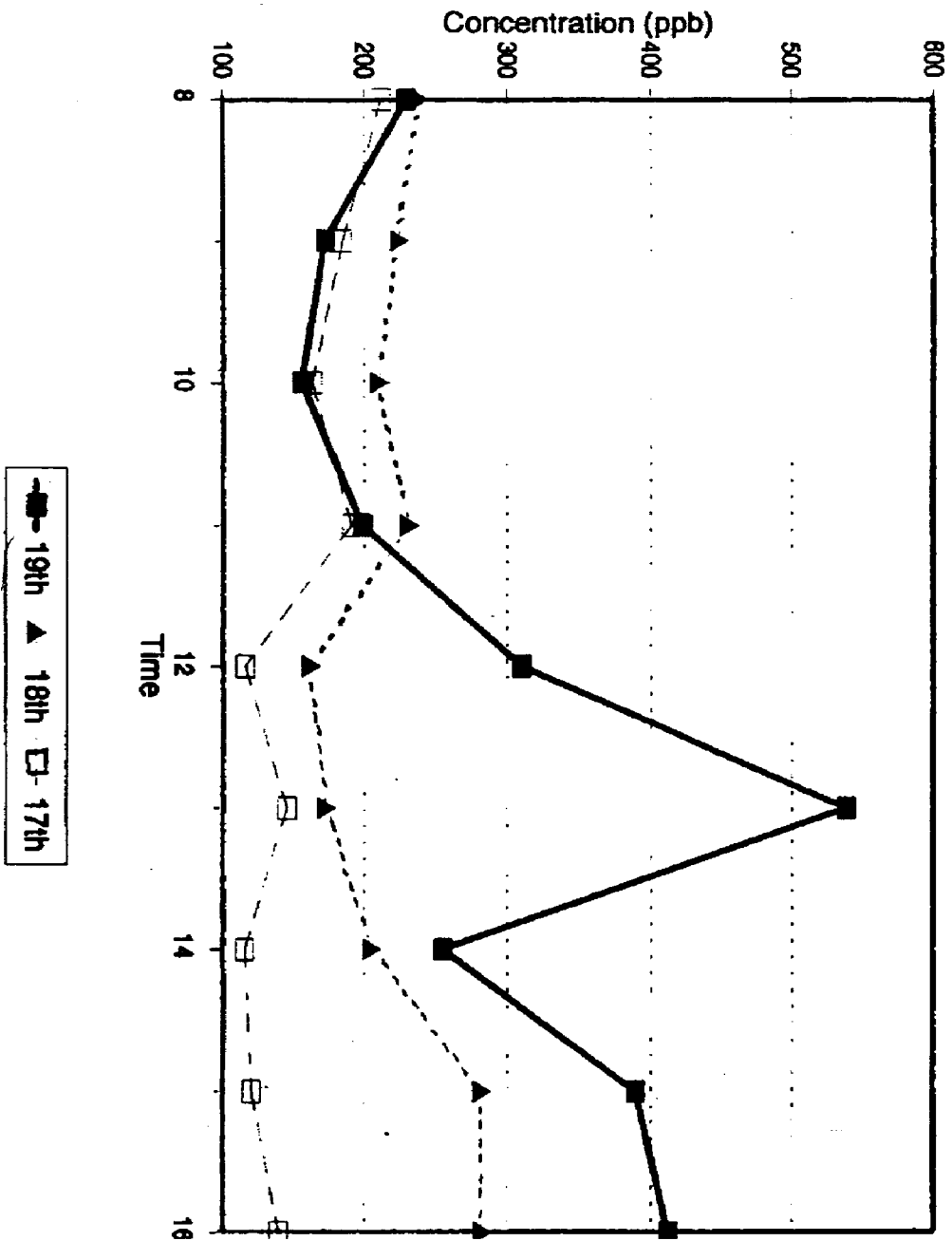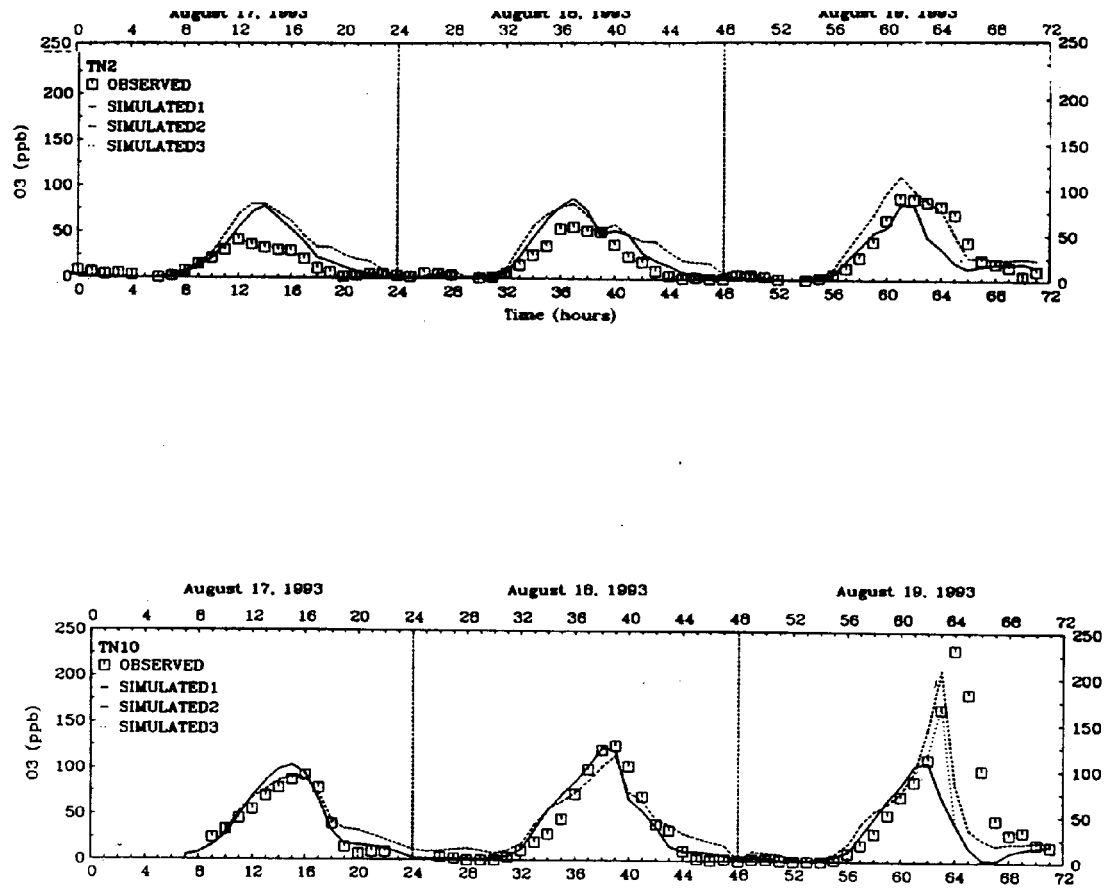
Figure 2-7. Time series plots of ozone at two sites before and after correction in emissions. Notice that simulated ozone changed significantly at site TN10, responding to emissions change, and little change occurred at site TN2 (top).
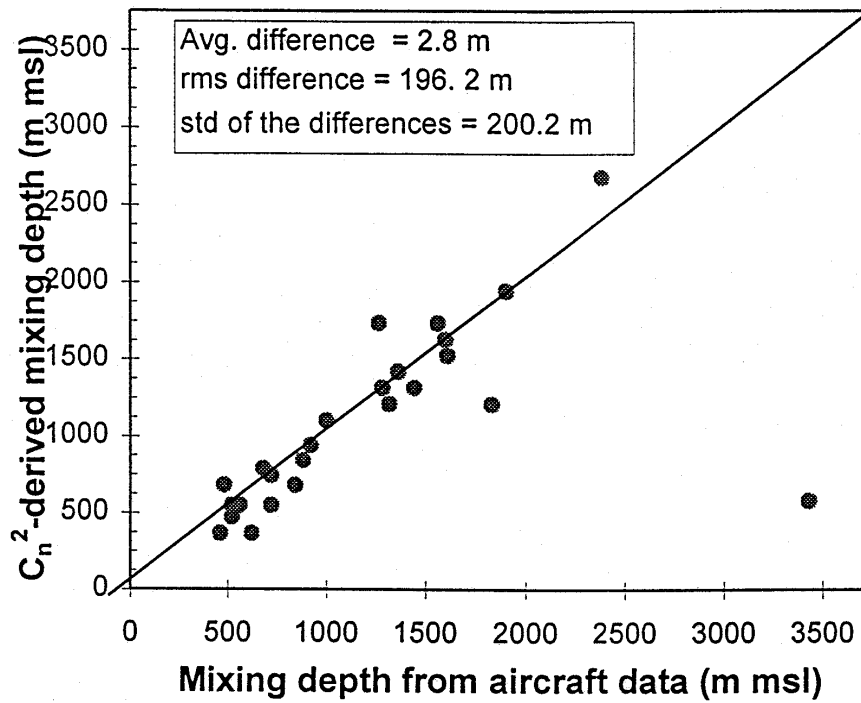
Figure 2-8. Scatter plot of C_N^2 derived mixing depths estimated from aircraft profiles of pollutant concentrations, turbulence and temperature. Twenty five comparisons were made using aircraft data collected in the afternoon near three profilers in southeast Texas (SAI, 1995).
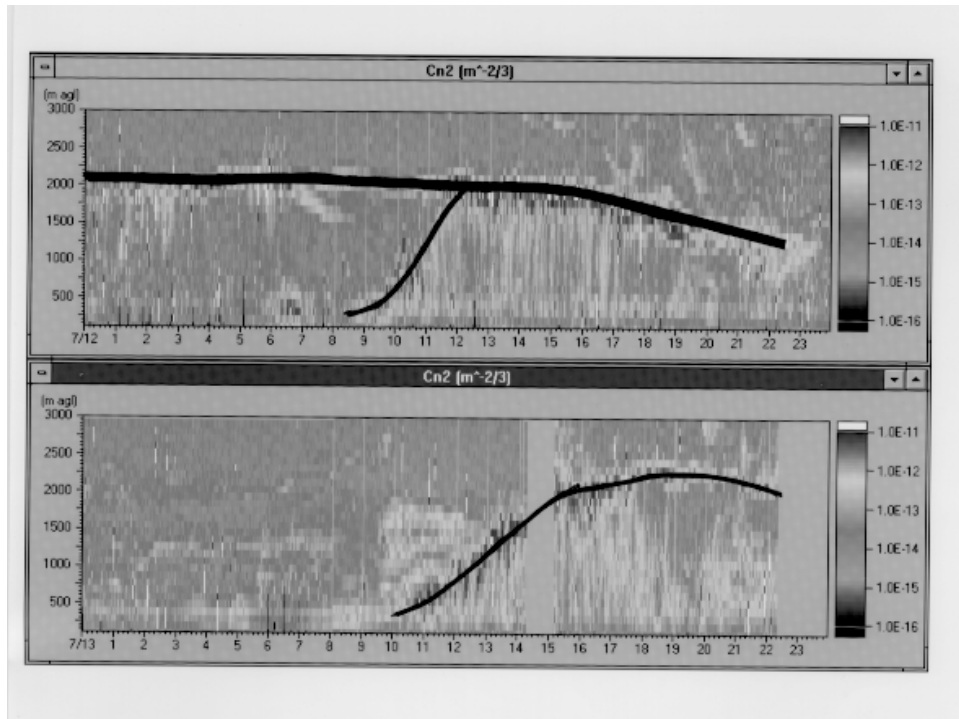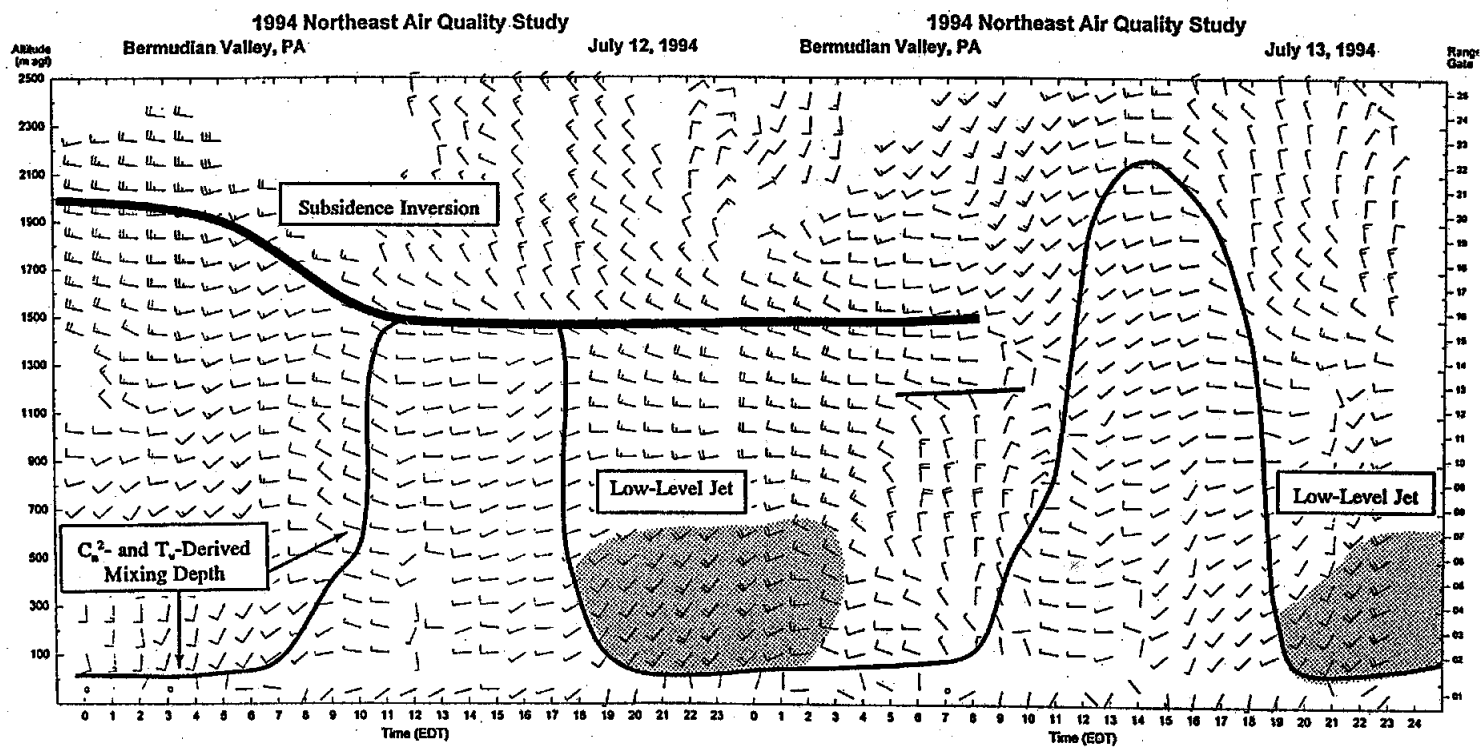
Figure 2.9   Time-height cross-section of C_N^2 for July 12-13, 1994 at New
Brunswick, NY. Thick line denotes the subsidence inversion; thin
line during the day denotes the top of the mixed layer. On July 12,
a subsidence inversion is shown in the profiler data as a region of
high reflectivity between 1750 and 2000 m agl. The inversion
limited afternoon growth of the CBL to below 2000 m. A slower
growth occurred on July 13 resulting in reduced vertical mixing of
precursors, and an attendant elevated afternoon ozone level.
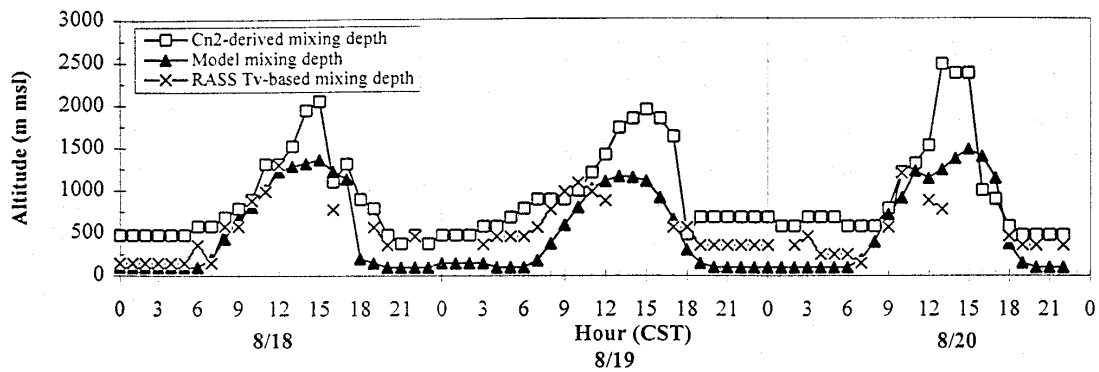
Figure 2.10   Time series plot of mixing depths estimated from C_N^2 and T_V data from a
meteorological model for a radar profiler site in Houston, TX for August 18-20,
1993 (Dye, et al. 1995).

Figure 2-11. Time-height cross-section of winds on July 12-13, 1994 at Bermudian Valley, PA, indicating jet formation and mixing depths. Each wind barb indicates direction and speed.

Table 2-1. Factors Affecting Weight of Evidence and Acceptance of Model
Results Nearly Passing the Attainment Test

Type of Analysis	Factors Increasing Weight of Evidence	Factors Supporting Deviation from Test Benchmark(s)
Photochemical Grid Model	-good performance -extensive data base -short projection period -confidence in inventories & projections	-overpredictions -major improvement in predicted AQ using a variety of indicators -results come very close to meeting the benchmark(s) -other peer-reviewed grid models predict comparable or better improvement in ozone
Trend Data	-extensive monitoring network -precursor & ozone trends avail. -statistical model normalizing trend explains much variance -little bias in statistically predicted highest ozone -short projection period -pronounced, stat. significant normalized trend -continued, comparable relative reductions in emissions provided for	-pronounced downward normalized trend exceeding that anticipated with grid model

Observational Models	-extensive monitoring network -QA'd, self-consistent results -plausible, physical explanations for findings	-indicates sources other than those in modeled strategies play significant roles
Selected Episodes	-all met.regimes corresponding w. high obs. O3 considered -met.ozone potential of episodes exceeded ~ 1/year	-observed O3 >> design value -Severity of met. conditions expected to be exceeded << 1/yr
Incremental Costs/Benefits	-good documentation for cost estimates -lack of alternatives for reducing emissions -lack of model responsiveness for variety of strategies as benchmark is approached	-lack of model responsiveness accompanied by high incremental costs
Other (optional) Analyses	-rationale documented	